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# **CORROSION93**

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## THE INTERRELATIONSHIP BETWEEN MARINE BIOFOULING AND CATHODIC PROTECTION

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### ABSTRACT

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Microorganisms colonize and form a gelatinous biofilm on all engineering materials exposed in natural marine environments, including cathodically protected surfaces. The impact of cathodic protection potentials on the chemical/biological composition of the biofilm and the impact of the biofilms on potentials required for cathodic protection have been the subject of numerous recent investigations. Literature on these subjects will be reviewed with emphasis on clarifying interactions between living and non-living deposits on cathodically protected metal surfaces.

**Keywords:** Cathodic protection, biofouling, calcareous deposits, biofilm

### INTRODUCTION

The corrosion of metallic structures exposed to seawater is frequently controlled by a process known as cathodic protection (CP) whereby a cathodic reaction is forced to occur everywhere on the exposed surface of the structure. CP can be achieved either by imposing a cathodic potential on the surface by means of an impressed direct current, attachment to a sacrificial anode, or both. The cost of CP is directly related to the amount of applied electrical current required to maintain the cathodic reaction. The amount of current required depends on the thickness, structure, and composition of films that either form on the metal surface or that are applied. For example, paints can be applied to metal surfaces to decrease the cost of CP. Corrosion products, calcareous deposits, and biofilms that form on cathodically protected surfaces also influence the current density required to maintain protective cathodic potentials.

Dexter<sup>1</sup> reviewed the mechanism of impressed current CP. Other investigators have evaluated the effect of seawater chemistry,<sup>2</sup> temperature,<sup>3</sup> exposure time,<sup>4</sup> velocity,<sup>5</sup> and other factors affecting formation of calcareous deposits during cathodic polarization.

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An impressed cathodic potential forces the following reactions:



These reactions cause an increase in alkalinity that forces a shift in the equilibria of all chemical reactions involving calcium, magnesium, and bicarbonate ions:



### Biofilms and Calcareous Deposits

In the following discussion all potentials have been reported in reference to a saturated calomel electrode (SCE). It has been reported that CP retards microbial growth because of the alkaline pH generated at the surface by reactions (1) and (2). Littauer and Jennings retarded biofouling in seawater using pulsed cathodic polarization of steel.<sup>6</sup> Dhar demonstrated that a potential more negative than -1024 mV was effective in decreasing bacterial content on titanium in seawater by 1 to 2 orders of magnitude.<sup>7</sup> The author concluded that in some systems it would be possible to prevent fouling and corrosion simultaneously by proper manipulation of the cathodic potential. However, numerous investigators have demonstrated a relationship between marine fouling and calcareous deposits on cathodically protected surfaces. For example, Mansfeld et al. polarized three stainless steels and titanium to -850 mV in natural Pacific seawater and followed the formation of surface layers using electrochemical impedance spectroscopy (EIS) and environmental scanning electron microscopy.<sup>8</sup> The applied potential was removed the day before EIS measurements, so that EIS data were collected at  $E_{\text{corr}}$  in a frequency range between 65 kHz and 10 or 1 mHz with a signal amplitude of 10 mV. Calcareous deposits and bacteria were evident on the surface after 5 days. Areal coverage of the surfaces could be followed with EIS (Figure 1a). For an exposure time of 5 days EIS data were similar for polarized and unpolarized samples (Figure 1b) despite the occurrence of scattered calcareous deposits on the polarized surface. After 13 days there were two time constants in EIS spectra of polarized samples indicating two surface conditions i.e., covered and uncovered. The occurrence of two time constants corresponding to calcareous deposits and uncovered surface is evident in the frequency dependence of the phase angle. After 43 days the time constants were no longer well defined due to complete coverage of polarized surfaces with calcareous deposits (Figure 2). In all cases bacterial cells could be imaged between and on top of calcareous deposits (Figure 3). It is noteworthy that the size and shape of calcareous deposits on polarized titanium differed from those on polarized stainless steel.

Despite the overwhelming evidence that bacteria and calcareous deposits coexist on cathodically protected surfaces, their interrelationships are not understood. Often microbiological data for cathodically polarized surfaces are confusing and impossible to compare because of the differing experimental conditions (laboratory vs. field) and techniques used to evaluate the constituents within the biofilm. It is further confusing because Edyvean et al. reported differences in current density, electrochemistry, calcareous deposits and biofilm formation due to varying organic content of seawater.<sup>9</sup>

Dexter et al. investigated the influence of a preexisting biofilm on the formation of calcareous deposits under cathodic protection in natural seawater.<sup>10</sup> They demonstrated that applied current densities up to  $100 \mu\text{A cm}^{-2}$  did not remove attached biofilms from stainless steel surfaces. Both natural marine and laboratory cultures changed the morphology of calcareous deposits formed under cathodic polarization at a current density of  $100 \mu\text{A cm}^{-2}$ .

Most investigators have evaluated the interrelationships of calcareous deposits and bacteria with respect to sulfate-reducing bacteria (SRB). SRB are ubiquitous, but they predominate in anaerobic marine biofilms because of the presence of  $2.5 \text{ gm l}^{-1}$  sulfate in seawater and the ability of some SRB to use hydrogen produced by acetogenic bacteria, enabling

them to outcompete other species. SRB within biofilms can reduce sulfate to sulfide that reacts with the metal surface to form corrosion products. SRB co-exist with numerous other organisms within biofilms, but because they are easily cultured and because their presence has been identified in numerous corrosion failures, SRB have unfortunately become indicator organisms for microbiologically influenced corrosion. Little and Wagner reviewed commercially available techniques for quantifying SRB and found orders of magnitude differences among techniques using the same sample.<sup>11</sup>

De Mele recently reported a dramatic decrease in bacterial populations due to cathodic protection after three hours immersion of a stainless steel in pure cultures of *Vibrio alginolyticus* in the laboratory.<sup>12</sup> However, after nine hours there were no significant differences in numbers of SRB on polarized and unpolarized surfaces. Cell numbers were evaluated using epifluorescence microscopy and standard plate counts. Nekoksa reported that cathodic potentials to -1000 mV caused a decrease in pH and an increase of SRB on carbon steel and 304L stainless steel surfaces.<sup>13</sup> At potentials more negative than -1000 mV, the pH became more alkaline and SRB numbers decreased. A study of the influence of SRB in marine sediments using EIS to monitor corrosion and lipid analysis as biological markers, complemented by chemical and microbiological analysis, showed that -880 mV encouraged growth of hydrogenase-positive bacteria in the sediment surrounding the metal and facilitated the growth of other SRB species.<sup>14</sup>

Because the enumeration technique strongly influences the number of cells one is able to count and because the number of cells cannot be equated to cellular activity, including sulfate reduction, some investigators have attempted to measure cellular activity on cathodically protected surfaces. Maxwell cathodically protected 50D mild steel (BS 4360) coupons exposed in the estuarine waters of Aberdeen Harbor using an imposed potential of -1024 mV and sacrificial anodes.<sup>15</sup> Activities within biofilms were determined using radiorespirometric methods. Biofilms developed on all cathodically protected and control unprotected substrata. The activities of aerobic and anaerobic bacteria, including SRB, were significantly greater on unprotected coupons. Furthermore, sulfide, a metabolic fingerprint of SRB activity, could only be detected in biofilms on unprotected coupons. These results show that a potential of -1024 mV does not prevent SRB from developing on cathodically protected surfaces. The lower activity of SRB within biofilms on cathodically protected coupons was not directly caused by any inhibitory effect of the cathodic potential. Instead, the greater activity of SRB on unprotected coupons was the result of production of an extensive corrosion film offering more favorable anaerobic conditions.

### Biofilms and Cathodic Protection

NACE Standard RP-01-69 lists cathodic protection criteria for underground or submerged steel, cast iron, aluminum and copper structures.<sup>16</sup> Microbiologically influenced corrosion is cited in paragraph 6.5.2 as "one of several abnormal conditions which sometimes exist and where cathodic protection is ineffective or only partially effective." It is important to point out that in the studies of Guezennec,<sup>14</sup> de Mele,<sup>12</sup> Dexter<sup>9</sup> and Nekoksa<sup>13</sup> SRB were present but accelerated corrosion was not reported.

Horvath and Novak studied thermodynamic data with iron in a pH 7 electrolyte saturated with H<sub>2</sub>S. A potential of -1024 mV was required to achieve cathodic protection.<sup>17</sup> Jack et al. demonstrated that -1024 mV was capable of providing cathodic protection in the presence of active SRB.<sup>18</sup> The influence of cathodic protection on the growth of SRB and on corrosion of steel in marine sediments was investigated by Guezennec and Therene.<sup>19</sup> They concluded that a cathodic potential of -880 mV did not appear to be sufficient for protection and that large amounts of cathodically produced hydrogen promoted the growth of SRB in the sediments surrounding the samples. Fischer conducted laboratory tests in anaerobic, artificial sediments containing SRB.<sup>20</sup> Results indicated that the criterion of -1024 mV for protection is adequate. Cathodic protection current density was between 4.5 and 12 mA ft<sup>-2</sup>. Pritula et al. indicated that a cathodic potential of -1054 mV lowered the corrosion rate of steel by 82.7% even though protective potentials in range -774 to -1134 mV did not inhibit growth of SRB.<sup>21</sup> Barlo and Berry concluded that if anaerobic bacterial activity is suspected, a cathodic polarization shift of approximately 200-300 mV is required for carbon steel protection.<sup>22</sup>

Little et al. showed that cathodically protected stainless steel surfaces in artificial seawater can become colonized by aerobic, acid-producing bacteria.<sup>23</sup> Formation of calcareous deposits and initial settlement of microorganisms resulted in decreased current density required to maintain a protection potential. Subsequent colonization and pH changes destabilized the calcareous deposits and dramatically increased current density required to maintain the imposed potential (Figures 4, 5). Ulanovski and Ledenev imposed cathodic protection on steel surfaces actively corroding in cultures of SRB and concluded that cathodic protection in the presence of SRB decreased corrosion by a factor of eight or nine.<sup>24</sup>

## SUMMARY

In summary, bacteria can be demonstrated on cathodically protected surfaces. Cathodic potentials to  $-1074$  mV did not prevent biofilm formation. It has been suggested that actual cell numbers may be related to polarization potential, dissolved organic carbon or to the enumeration technique. Numbers of SRB may be increased or decreased depending on exposure conditions. Carbon steel is considered protected when a potential of  $-924$  mV is achieved. In many cases, the potential is further reduced to  $-1024$  mV to protect the steel from corrosion caused from the activity of SRB. The decreased potential is not applied to prevent growth of SRB, but is based on a theoretical level which will allow passivity of steel in a sulfide-rich environment produced by SRB. The main consequence of biofilm formation on protected surfaces appears to be an increase in the current density necessary to polarize the metal to the protection potential. The presence of large numbers of cells on cathodically protected surfaces does mean that in the event that cathodic protection is intermittent, discontinuous, or discontinued, the corrosion attack due to the microorganisms will be more aggressive.

## ACKNOWLEDGMENTS

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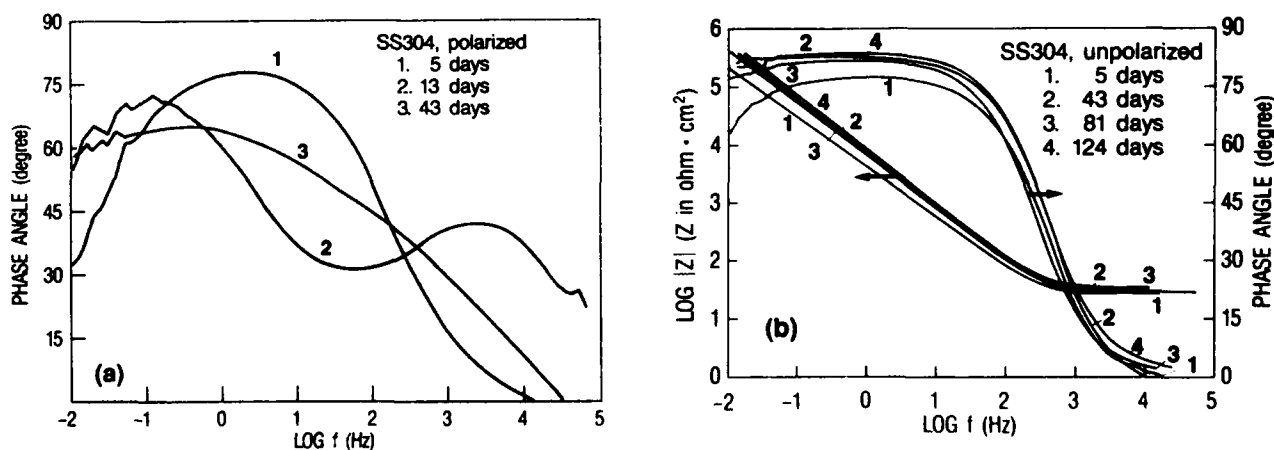


FIGURE 1 – (a) Impedance spectra for polarized 304 stainless steel (EIS data measured at  $E_{\text{corr}}$ ) and (b) impedance spectra for unpolarized 304 stainless steel

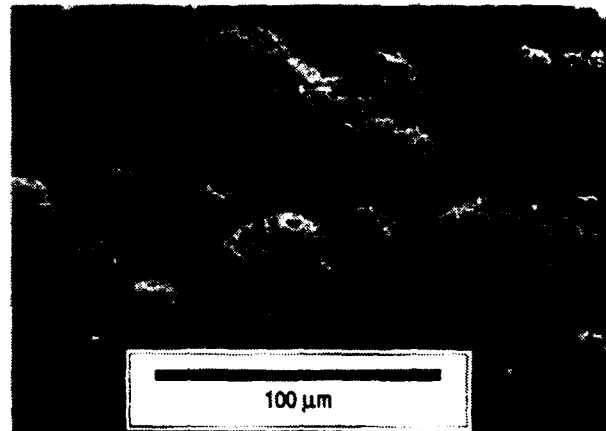


FIGURE 2 – Calcareous deposits on polarized 304 stainless steel after 43 days

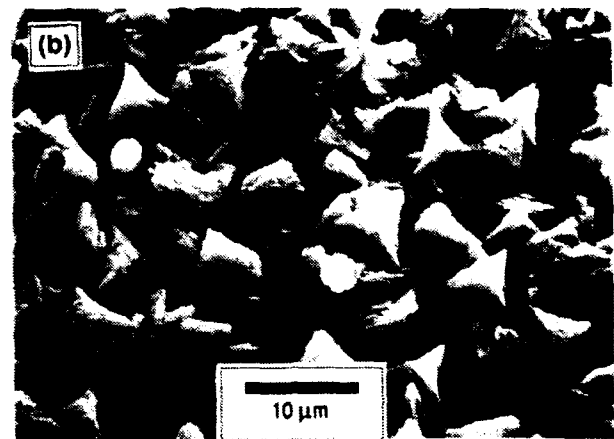
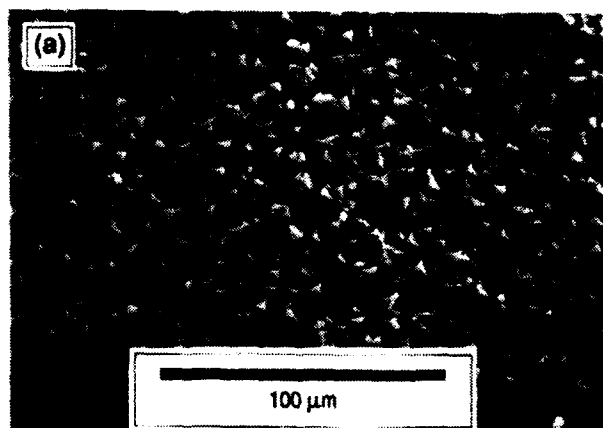


FIGURE 3 – (a), (b) calcareous deposits on polarized titanium (grade 2) after 43 days, and (c) bacteria between calcareous deposits

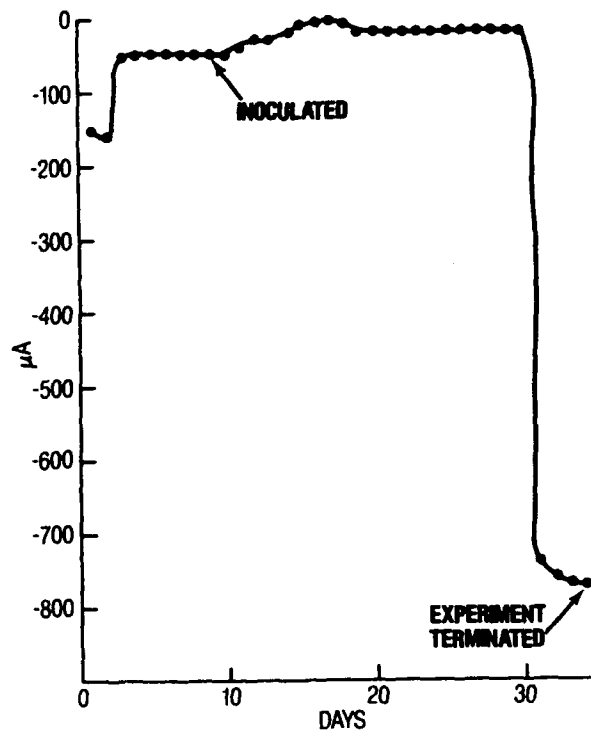


FIGURE 4 – Current density required to maintain  $-900$  mV (SCE) vs time

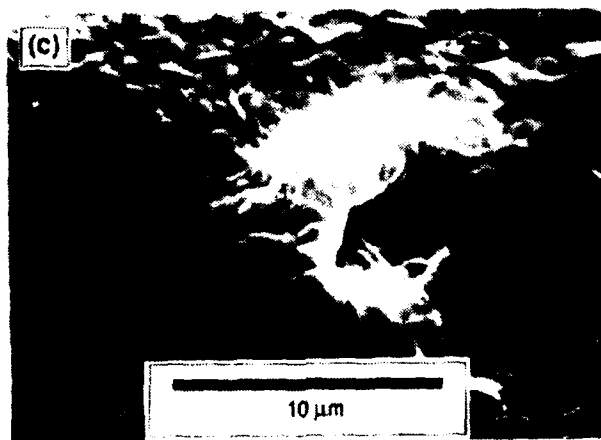
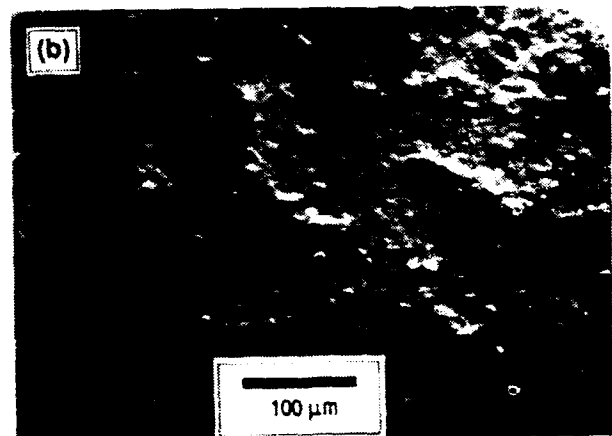


FIGURE 5 – Stainless steel polarized  $-900$  mv (SCE): (a) colonized electrode surface, (b) colonized pitted electrode, and (c) pits and associated bacteria